

# Single Determinant Basis Set for the Non-Relativistic Electronic Schrödinger Equation Using the Coupling Strength Parameter Generalized Brillouin Theorem

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**Abstract.** The Brillouin theorem has been generalized for the coupling strength parameter ( $a$ ) extended non-relativistic electronic Hamiltonian ( $H_V + H_{ne} + aH_{ee}$ ). The mathematical case  $a=0$  generates an orthonormalized set of single Slater determinants which can be used as basis set for configuration interactions (CI) calculations for the physical case  $a=1$ , removing the known restriction by the original Brillouin theorem and opening a new way to practice.

**Keywords.** electron-electron repulsion energy participation in ground and excited states, coupling strength parameter, totally non-interacting reference system, generalization of Brillouin theorem, single determinant basis set, configuration interactions

## INTRODUCTION: Coupling strength parameter as input

The non-relativistic, spinless, fixed nuclear coordinate electronic Schrödinger equation for a molecular systems of  $M$  atoms and  $N$  electrons with nuclear configuration  $\{\mathbf{R}_A, Z_A\}_{A=1,\dots,M}$  in free space is

$$H(a) y_k \equiv (H_V + H_{ne} + aH_{ee}) y_k(\mathbf{x}_1, \dots, \mathbf{x}_N) = \text{enrg}_{\text{electr},k} y_k(\mathbf{x}_1, \dots, \mathbf{x}_N) \quad (1)$$

where  $y_k$  and  $\text{enrg}_{\text{electr},k}$  are the  $k^{\text{th}}$  excited state ( $k=0,1,2,\dots$ ) anti-symmetric wave function (with respect to all spin-orbit electronic coordinates  $\mathbf{x}_i \equiv (\mathbf{r}_i, s_i)$ ) and electronic energy, respectively, as well as the electronic Hamiltonian operator contains the sum of kinetic energy, nuclear–electron attraction and electron–electron repulsion operators, the latter is extended with coupling strength parameter ( $a$ ). Only  $a=1$  makes physical sense (!), while the case  $a=0$  mathematically provides a good starting point to solve the case  $a=1$ . Most popular approximations [1, 2] are the expensive but (chemical) accurate CI method for ground and excited states, the less accurate but faster and less memory taxing Hartree–Fock self consistent field (HF-SCF) method for ground state with or without correlation corrections, and the density functional theory (DFT, using HF-SCF framework) [3]. The CI works for any nuclear geometry, while the HF-SCF is only for the vicinity of stationary points using a single Slater determinant. The “ $a$ ” connects an unphysical system ( $H(a=0)$ ) to the system treated at the mean-field HF level ( $H(a=1)$ ) and above and its effect on ground and excited states. For example, a bit below unity “ $a$ ” is capable [4] to correct the HF-SCF energy remarkably.

The  $(y_k(a), \text{enrg}_{\text{electr},k}(a))$  is the  $k$ -th eigenvalue pair of  $H(a)$ , and we distinguish notations for  $a=0$  as  $(Y_k, \text{e}_{\text{electr},k})$  and for  $a=1$  as  $(\Psi_k, E_{\text{electr},k})$ . The  $S_0$  (generally  $s_0(a)$ ) is a single determinant approximation for  $\Psi_0$  (generally for  $y_0(a)$ ) via HF-SCF/basis/ $a=1$  (generally “ $a$ ”) energy minimizing algorithm. Fundamental is that the  $y_k(a=0)=Y_k$  is a single determinant form solution, while  $y_k(a \neq 0)$  is not.  $E_{\text{electr},0}(\text{method})$  approximates  $E_{\text{electr},0}$  by a certain method (HF-SCF, CI, etc.). The standard HF-SCF routine (Gaussian pre-package) was modified with a few simple program lines, which calls for the subroutine to calculate the  $\langle S_0 | H_{ee} | S_0 \rangle$ . Simply, the seed term  $r_{ij}^{-1}$  was overwritten with  $ar_{ij}^{-1}$ , and the parameter “ $a$ ” was programmed as input (see Appendix 1).

## DISCUSSION: The totally non-interacting reference system

Similarly to  $a=1$ , for  $a=0$  we ask  $Y_k$  to be anti-symmetric and well behaving (vanishing at infinity and square-integrable), normalized as  $\langle Y_k | Y_k \rangle = 1$ , calling “totally non-interacting reference system” (TNRS) in analogy to the corresponding anti-symmetric and well behaving  $\Psi_k$  normalized as  $\langle \Psi_k | \Psi_k \rangle = 1$ . Certain theorems for  $a=1$  hold for  $a=0$  as well. Both are linear partial differential equations, the variation principle holds, and the 1<sup>st</sup> (“TNRS one-electron density,  $\rho_0(\mathbf{r}_2, \text{TNRS})$ , defines  $Y_0$  and the nuclear frame”) and 2<sup>nd</sup> (“variation principle for TNRS one-

electron density in its DFT functional) Hohenberg – Kohn (HK) theorems hold. The energetically lowest lying eigenvalue pair ( $e_{\text{electr},0}, Y_0$ ) corresponds to ( $E_{\text{electr},0}, \Psi_0$ ) and  $E_{\text{electr},0} \gg e_{\text{electr},0}$  for any molecular system (in stationer or non-stationer geometry, because  $1/r_{ij} \geq 0$  always). The ground state versus the energetically lowest lying state with an enforced spin multiplicity feature is also the same in HF-SCF/basis/a. However, if spin-spin interaction is not considered via Coulomb repulsion, Hund's rule does not apply if  $a=0$  but does if  $a \neq 0$ . There are major mathematical differences between  $a=0$  and  $a \neq 0$  aside from the visible inclusion vs. omitted operator  $H_{\text{ee}}$ : It is responsible for the fact that a single Slater determinant  $S_0$  for  $\Psi_0$  when  $a=1$  (generally  $a \neq 0$ ) is not enough for total accuracy, although in the vicinity of stationary points, it provides a good approximation, and it can provide many characteristic properties of the ground state eigenvalue. In contrast, a single Slater determinant form is adequate form if  $a=0$  not only for the ground, but also for excited states, and the HF-SCF/basis/a=0 with basis set limit accurately calculates the eigenvalue pairs ( $e_{\text{electr},k}, Y_k$ ) for ground and excited states.

For Eq.1: Analytical solution exists for  $k \geq 0$  if  $N=1$  ( $\Rightarrow H_{\text{ee}}=0$ ) and  $M=1$ , e.g.  $\Psi_0 = c \cdot \exp(-Z/r_1)$ ; If  $k \geq 0 \Rightarrow$  single Slater determinant is a correct form if  $a=0$ , but incorrect if  $a=1$ . The HF-SCF/basis/a algorithm provides single Slater determinants for the two important cases ( $Y_0$  ( $a=0$ ),  $S_0$  ( $a=1$ )), to approximate the solutions of Eq.1 for ground state  $k=0$  (or lowest lying enforced spin multiplicity state) as well as excited states ( $k > 0$ ,  $Y_k$  ( $a=0$ ),  $S_k$  ( $a=1$ )) can be generated with “tricks”. The HF-SCF/basis/a algorithm owns the properties: Energy variation principle holds for any “a”. Surprisingly,  $Y_0$  is very close [5] to  $S_0$ .  $\Psi_k \approx S_k$  is “good” approx. for  $k=0$  only.  $Y_0$  is not restricted to the vicinity of the stationary point, but  $S_0$  does (by  $1/r_{ij}$ ). If  $a=0 \Rightarrow$  there is basis set error, but no correlation effect (notation  $Y$  only); if  $a \neq 0 \Rightarrow$  there is correlation and basis set error (we distinguish  $\Psi$  and  $S$  to emphasize). Case  $a=0$  provides a very rich pro-information for  $a=1$  and faster (the need of SCF convergence by  $1/r_{12}$  is eliminated). This new orthonormal basis set  $\{Y_k\}$  provides simpler Hamiltonian matrix for different level CI calculations in its off-diagonal elements than the  $\{S_k\}$ , see Eq.4, along with an opportunity to avoid the restriction from Brillouin's theorem [1, 5].

The un-coupled case  $a=0$ , i.e.  $(H_V + H_{\text{ne}})Y_k = -(1/2)\sum_{i=1,\dots,N} \nabla_i^2 - \sum_{i=1,\dots,N} \sum_{A=1,\dots,M} Z_A R_{Ai}^{-1} Y_k = \sum_{i=1,\dots,N} n_i h_i = e_{\text{electr},k} Y_k$ , decomposes to  $N$  one-electron equations as the coupled case  $a \neq 0$  (in the Fock (HF) or Kohn Sham (KS) formalisms  $a=1$ ), that is  $(h_1 + a V_{\text{ee,eff}}(\mathbf{r}_i)) \phi_i(\mathbf{r}_i) = \epsilon_i \phi_i(\mathbf{r}_i)$ , where  $\phi_i(\mathbf{r}_i)$  are the ortho-normal molecular orbits (MOs, with  $\langle \phi_i | \phi_j \rangle = \delta_{ij} \equiv$  Kronecker delta), and e.g.  $V_{\text{ee,eff}}(\mathbf{r}_i) = \int \rho_0(\mathbf{r}_2, \text{KS}) r_{i2}^{-1} d\mathbf{r}_2 + V_{\text{xc}}(\mathbf{r}_i)$  is the effective potential from electron-electron repulsion: The operator seed  $1/r_{ij}$  is reduced to the variable  $\mathbf{r}_i$  via performing the integrations, and virtually (!) all equations depend on one electron. It is in fact coupled, though virtually not coupled, so the 100% adequate anti-symmetric solution for this equation system (but not for  $a=1$  in Eq.1) is a Slater determinant, and this system is known as “non-interacting reference system”; if  $a=0$  also holds (really un-coupled), we call it TNRS. The electronic energy is  $e_{\text{electr},k} = \sum_i n_i \epsilon_i$ , where  $n_i$  is the population (0, 1 or 2), and  $\sum_i n_i = N$  for ground and excited states in contrast to  $E_{\text{electr},0}(\text{HF-SCF or KS/basis/a=1}) \neq \sum_i n_i \epsilon_i$  for deepest possible filling in the single Slater determinant (some cross terms must be subtracted). For a value of  $N$  and multiplicity  $2S+1 = 2\sum_i s_i + 1$  in the regular way, the HF-SCF/basis/a=0 calculates the lowest lying  $N/2$  or  $(N+1)/2$  energy values ( $\epsilon_i$ ) and MOs ( $\phi_i$ ), the only error is the basis set error, while HF-SCF/basis/a=1 (or  $\neq 0$ ) optimizes an  $S_0$  (or  $s_0$ ) single determinant energetically, keeping MOs of  $S_0$  (or  $s_0$ ) ortho-normal owning basis set and correlation error. The linear combination of atomic orbits (LCAO) coefficients of TNRS can be obtained in only one step with HF-SCF/basis/a=0, irrespective of system size (via eigensolving), while in the HF-SCF/basis/a=1 the LCAO coefficients for a real system (or the mathematical  $a \neq 0$  cases) can only be obtained through many steps; operator  $aH_{\text{ee}}$  is responsible for this, and the number of steps dramatically increases with system size ( $N$ ).

An important link between  $a=0$  and  $1$  comes from  $\langle \Psi_0 | H_{\text{ee}} | Y_0 \rangle = \langle \Psi_0 | H(a=1) - (H_V + H_{\text{ne}}) | Y_0 \rangle = \langle \Psi_0 | H | Y_0 \rangle - \langle \Psi_0 | (H_V + H_{\text{ne}}) | Y_0 \rangle = \langle Y_0 | H | \Psi_0 \rangle - e_{\text{electr},0} \langle \Psi_0 | Y_0 \rangle = E_{\text{electr},0} \langle Y_0 | \Psi_0 \rangle - e_{\text{electr},0} \langle \Psi_0 | Y_0 \rangle$  as

$$E_{\text{electr},0} = e_{\text{electr},0} + \langle \Psi_0 | H_{\text{ee}} | Y_0 \rangle / \langle \Psi_0 | Y_0 \rangle. \quad (2)$$

The ratios  $\langle \Psi_0 | H_{\text{ee}} | Y_0 \rangle / \langle \Psi_0 | Y_0 \rangle$  and  $(E_{\text{electr},0} - e_{\text{electr},0}) / e_{\text{electr},0}$  are quasi-constants as a function of molecular frame seeded in operator  $H_{\text{ne}}$ . (Compare to the virial theorem  $(V_{\text{nn}} + V_{\text{ne}} + V_{\text{ee}}) / T = -2 = (V_{\text{nn}} + V_{\text{ne}}) / T \equiv (V_{\text{nn}} + \langle Y_0 | H_{\text{ne}} | Y_0 \rangle) / \langle Y_0 | H_V | Y_0 \rangle$  which holds exactly on atoms.) Difference is between  $V_{\text{ee}} \equiv \langle \Psi_0 | H_{\text{ee}} | \Psi_0 \rangle = (N(N-1)/2) \langle \Psi_0 | r_{12}^{-1} | \Psi_0 \rangle$  and the corresponding  $\langle \Psi_0 | H_{\text{ee}} | Y_0 \rangle / \langle \Psi_0 | Y_0 \rangle = (N(N-1)/2) \langle \Psi_0 | r_{12}^{-1} | Y_0 \rangle / \langle \Psi_0 | Y_0 \rangle$ . The  $E_{\text{total electr},0} - e_{\text{total electr},0} = E_{\text{electr},0} - e_{\text{electr},0}$ , because the nuclear-nuclear repulsion energy,  $V_{\text{nn}}$ , cancels. Between  $k$  and  $k'$  excited states  $E_{\text{electr},k} = e_{\text{electr},k'} + (N(N-1)/2) \langle \Psi_k | r_{12}^{-1} | Y_{k'} \rangle / \langle \Psi_k | Y_{k'} \rangle$ . The LCAO coefficients in  $S_0$  and  $Y_0$  are very close to each other (aside from phase factors, see Appendix 2) so from Eq.2

$$E_{\text{electr},0} \approx E_{\text{electr},0}(\text{TNRS}) = e_{\text{electr},0} + (N(N-1)/2) \langle Y_0 | r_{12}^{-1} | Y_0 \rangle. \quad (3)$$

Extension of the 1<sup>st</sup> Hohenberg-Kohn (HK) theorem:  $Y_0(a=0) \Leftrightarrow H_{\text{ne}} \Leftrightarrow \Psi_0(a=1)$ , generally  $y_0(a) \Leftrightarrow H_{\text{ne}}$ .

For excited states  $\{Y_k(a=0)\}$ : 1.: One has to provide basis set adequate for higher  $\phi_i$  ( $i > N/2$  or  $(N+1)/2$ ) states, 2.: Simply increase the  $N$  by e.g. 1 or 2 for the same nuclear frame in HF-SCF/basis/ $a=0$ . This  $\{Y_k(a=0)\}$  determinant basis set can be used for CI calculations, as the  $\{S_k(a=1)\}$  in practice, the linear algebra is exactly the same, but the algebraic forms do differ a slightly. The orthogonal property is  $\langle \phi_i(\mathbf{r}_1) | \phi_j(\mathbf{r}_1) \rangle = \langle Y_i(\mathbf{x}_1, \dots, \mathbf{x}_N) | Y_j(\mathbf{x}_1, \dots, \mathbf{x}_N) \rangle = \delta_{ij}$ , where the integration means 3 and 4N dimensions, resp. in bra-kets; also,  $\langle \Psi_k | \Psi_{k'} \rangle = \langle Y_k | Y_{k'} \rangle = \delta_{kk'}$  or  $\approx \langle \Psi_k | Y_{k'} \rangle$ . Normalization  $N \langle Y_i | Y_i \rangle = \int \rho_i(\mathbf{r}_1, a=0) d\mathbf{r}_1 = N$  also holds, as a conventional definition for  $i^{\text{th}}$  excited state. From the hermetic and linear nature of the operators:  $\epsilon_j \delta_{ij} = \langle \phi_i | h_1 | \phi_j \rangle = \langle \phi_j | h_1 | \phi_i \rangle = \epsilon_i \delta_{ji}$  and  $e_{\text{electr},j} \delta_{ij} = \langle Y_i | H_V + H_{\text{ne}} | Y_j \rangle = \langle Y_j | H_V + H_{\text{ne}} | Y_i \rangle = e_{\text{electr},i} \delta_{ji}$  holds for orbital  $\{\phi_i(\mathbf{r}_1)\}$  and determinant  $\{Y_k\}$  sets, as well as  $\langle b_i | h_1 | b_j \rangle = \langle b_j | h_1 | b_i \rangle$  for basis set elements. A simple demonstration of this follows with  $\Sigma Z_A = N=10$  and singlet ( $1+2\Sigma s_i=1$ ) hydrogen-fluorid molecule (MP2(full)/6-31G\* geometry,  $E_{\text{total electr},0}(\text{MP2 level}) = -100.1841$  Hartree), the HF-SCF/STO-3G/ $a=1$  for  $(\Psi_0 \approx S_0, E_{\text{electr},k})$ , yields

```
1CLOSED SHELL SCF, NUCLEAR REPULSION ENERGY IS 5.099731703 HARTREES
0CONVERGENCE ON DENSITY MATRIX REQUIRED TO EXIT IS 1.0000D-05
0 CYCLE    ELECTRONIC ENERGY    TOTAL ENERGY    CONVERGENCE    EXTRAPOLATION
  1         -103.453458282         -98.353726579
  2         -103.658442376         -98.558710673    4.81239D-02
  . . . convergence . . .
  6         -103.671950402         -98.572218699    5.80744D-06
0AT TERMINATION TOTAL ENERGY IS          -98.572219 HARTREES
1MOLECULAR ORBITALS                      5 OCCUPIED MO
      EIGENVALUES---      1          2          3          4          5          6
1  1  F  1S      0.99472    -0.24986    0.08063    0.00000    0.00000    0.08298
2  1  F  2S      0.02247    0.94095   -0.42420    0.00000    0.00000   -0.53979
3  1  F  2PX     0.00000    0.00000    0.00000    0.28444   -0.95869    0.00000
4  1  F  2PY     0.00000    0.00000    0.00000    0.95869    0.28444    0.00000
5  1  F  2PZ    -0.00283   -0.08462   -0.70026    0.00000    0.00000    0.82101
6  2  H  1S     -0.00558    0.15494    0.52694    0.00000    0.00000    1.07402
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while the HF-SCF/STO-3G/ $a=0$  for  $(Y_0, e_{\text{electr},k})$  yields

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1CLOSED SHELL SCF, NUCLEAR REPULSION ENERGY IS 5.099731703 HARTREES
0CONVERGENCE ON DENSITY MATRIX REQUIRED TO EXIT IS 1.0000D-05
0 CYCLE    ELECTRONIC ENERGY    TOTAL ENERGY    CONVERGENCE    EXTRAPOLATION
  1         -151.075395174        -145.975663471
  2         -152.831334744        -147.731603041    0.00000D+00
0AT TERMINATION TOTAL ENERGY IS          -147.731603 HARTREES
1MOLECULAR ORBITALS                      5 OCCUPIED MO
      EIGENVALUES---      1          2          3          4          5          6
1  1  F  1S     -40.59236    -9.55517   -8.81672   -8.72571   -8.72571   -4.49671
2  1  F  2S      1.00121    0.23152    0.08800    0.00000    0.00000    0.03901
3  1  F  2PX     0.00000    0.00000    0.00000   -0.03804   -0.99928    0.00000
4  1  F  2PY     0.00000    0.00000    0.00000   -0.99928    0.03804    0.00000
5  1  F  2PZ     0.00024    0.44410   -0.94971    0.00000    0.00000    0.26910
6  2  H  1S      0.00188    0.20530   -0.09439    0.00000    0.00000    1.18497
```

Notice the similar LCAO coefficients, the different energy values, the different phase factors, (e.g.  $\text{sgn}(0.94095)$  vs.  $\text{sgn}(-1.03159)$  in 2<sup>nd</sup> MO ( $\phi_2(a), \epsilon_2(a)$ )), as well as case  $a=0$  has only one convergence step (#2) after initial guess (#1). Calculating higher MO or  $\phi_i$  (for generating e.g.  $Y_1$ ) one simply has to increase  $N$ , e.g. adding -1 charge to the molecule ( $N=11$ ), and using correct multiplicity (now  $1+2\Sigma s_i=2$ ): The HF-SCF/STO-3G/ $a=0$  calculation yields exactly the same LCAO coefficients and energy eigenvalues as for the neutral ( $N=10$ ) hydrogen-fluoride for the first 5 MOs, because it is the TNRS ( $a=0$ ) calculation; but instead of 5 doubly occupied MO (HOMO=5<sup>th</sup>, LUMO=6<sup>th</sup>), there are 5 doubly occupied MOs plus 1 singly occupied 6<sup>th</sup> MO (HOMO). In contrast, the HF-SCF/STO-3G/ $a=1$  (e.g. RHF) calculation yields different  $\{\epsilon_i, \phi_i\}$  set for  $i=1, \dots, 5$  if  $N$  increases to 11. After the name “virtual” MOs, this tricking in TNRS with  $N$  can have the name “virtual”  $N$ . One must be aware of the basis set chosen at this point to be good enough for the new HOMO too (to avoid singularity). Recall the Brillouin theorem (stated for  $a=1$ ): the CI basis set generation by HF-SCF/basis/ $a=1$  restricts stopping at single excitation (double excitation is necessary at least), while via HF-SCF/basis/ $a=0$  this restriction is removed, an important practical advantage beside the theoretically interesting generalization of Brillouin theorem with “ $a$ ” below. Finally, generating a basis set  $\{Y_k\}$  with a HF-SCF/basis/ $a=0$  is simpler, faster (one step), more effective (larger  $k$ ) and more convenient than generating set  $\{S_k\}$  with an HF-SCF/basis/ $a=1$ , although, the author knows perfectly well that the latter is effectively used and widely tested in practice. Additionally, in the case of  $a=1$  the LUMO and up bear the properties of  $S_0$ , passing it to

the ortho-normal basis set for the CI calculation it generates, but only  $S_0$  has a really close relationship to  $a=1$  in Eq.1, while on the other hand, in the case of  $a=0$  all  $Y_k$  are the solution of case  $a=0$  in Eq.1. The standard way of expanding anti-symmetric wave functions  $\Psi_K$  of  $a=1$  (most importantly to ground state  $K=0$ ) using the ortho-normal  $N$ -electron determinant basis set  $\{Y_k\}$  from  $a=0$  is the linear combination of single, double, triple, etc. excited  $N$ -electron Slater determinants:  $\Psi_K = \sum_k c_k(K) Y_k$ , as alternative to the conventional  $\Psi_K = \sum_k d_k(K) S_k$ ; ( $K$  distinguished from  $k$ ). By the principles of linear algebra, changing basis set should not be a problem, mainly from the point of slowly changing LCAO parameters in the range  $0 \leq a \leq 1$ . (The textbook routine generation of basis sets, e.g. for singlet excitation, is taking 5 columns from the 6 for a  $10 \times 10$  determinant  $Y_k$  or  $S_k$  in the above table.)

Standard linear algebra provides the set of eigenstates  $\{\Psi_K, E_{\text{electr},K}\}$  for  $a=1$  by expanding  $\Psi_K$  in basis set  $\{Y_k\}$ : One must diagonalize the Hamiltonian matrix  $\langle Y_{k'} | H_V + H_{ne} + H_{ee} | Y_k \rangle$  as the second main step. (The first main step is the diagonalization of  $\langle b_i | h_1 | b_j \rangle$  for the set of eigenstates  $\{Y_k, E_{\text{electr},k}\}$  with HF-SCF/basis/ $a=0$  with tricking (virtual)  $N$  if necessary.) Using general “ $a$ ”, not only  $a=0$  and 1, yields

$$\langle Y_{k'} | H_V + H_{ne} + a H_{ee} | Y_k \rangle = e_{\text{electr},k} \langle Y_{k'} | Y_k \rangle + a \langle Y_{k'} | H_{ee} | Y_k \rangle. \quad (4)$$

The diagonal elements ( $k'=k$ ) reduce to the generalization of Eq.3 for ground ( $k=0$ ) and excited ( $k>0$ ) states

$$\langle Y_k | H_V + H_{ne} + a H_{ee} | Y_k \rangle = e_{\text{electr},k} + a(N(N-1)/2) \langle Y_k | r_{12}^{-1} | Y_k \rangle, \quad (5)$$

$$E_{\text{electr},k} \approx E_{\text{electr},k}(\text{TNRS}) \equiv e_{\text{electr},k} + (N(N-1)/2) \langle Y_k | r_{12}^{-1} | Y_k \rangle. \quad (6)$$

Approximation Eq.6 is pre-tested: Its  $k=0$  case in Eq.3 is displayed on Fig.1. Ordering  $E_{\text{electr},k}$  as  $E_{\text{electr},k} \leq E_{\text{electr},k+1}$  for  $k=0,1,2,\dots$ , it must be proved that  $Y_k$  (case  $a=0$ ) corresponds to  $\Psi_k$  (case  $a=1$ ), which is a plausible hypothesis and agrees with Eq.6. (The “ $\leq$ ” necessary in energy relation, the “ $<$ ” is not enough, because TNRS can remove degeneracy gaps, manifesting in Hund’s rule extended with “ $a$ ”, moreover,  $\Psi_k$  can characteristically have degeneracy.) Algebraic theorem  $\Sigma(\text{eigenvalues}) = \text{trace} \equiv \Sigma(\text{diagonal elements})$  for symmetric matrices yields another relationship for terms in Eq.5. The off-diagonal elements ( $k' \neq k$ )

$$\langle Y_{k'} | H_V + H_{ne} + a H_{ee} | Y_k \rangle = e_{\text{electr},k} \text{ or } k' \langle Y_{k'} | Y_k \rangle + a \langle Y_{k'} | H_{ee} | Y_k \rangle = a(N(N-1)/2) \langle Y_{k'} | r_{12}^{-1} | Y_k \rangle \quad (7)$$

show purely Coulomb electron-electron interaction terms to correct Eq.6 by eigensolving Eq.4. In practice, where not the  $\{Y_k\}$  by HF-SCF/basis/ $a=0$ , but  $\{S_k\}$  by HF-SCF/basis/ $a=1$  is used, the off-diagonal elements corresponding to Eq.7 contain orbital energies  $\epsilon_i$  of MOs too. The CI matrix in Eq.4 is diagonal if  $a=0$ , because the set of wave functions  $\{Y_k\}$  is expressed trivially with itself. Neglecting off-diagonal elements (Eq.7), the matrix in Eq.4 diagonalizes to Eqs.5-6, see  $E_{\text{total electr},0}(\text{G3}) - E_{\text{total electr},0}(\text{TNRS})$  plotted with a solid line in Fig.1, which is remarkable but, far beyond chemical accuracy. The  $\langle Y_k | r_{12}^{-1} | Y_k \rangle$  terms generate many products, but the orthogonality of MOs in  $\{Y_k\}$  makes many cancellations; the spin related properties and manipulations are exactly the same in both,  $\{Y_k\}$  and  $\{S_k\}$ . To avoid eigensolving Eq.4, Eq.6 can be corrected e.g. with  $L^{\text{th}}$  order power series expansion as  $E_{\text{electr},0} \approx E_{\text{electr},0}(\text{TNRS}) + (a_1 t + b_1 v_{ne} + (c_1 - 1)z) + \sum_{j=2,\dots,L} (a_j t^j + b_j v_{ne}^j + c_j z^j)$ , where the pre-calculated  $t \equiv \langle Y_0 | H_V | Y_0 \rangle$ ,  $v_{ne} \equiv \langle Y_0 | H_{ne} | Y_0 \rangle$  and  $z \equiv a \langle Y_0 | H_{ee} | Y_0 \rangle$  integrals are used, etc..

Eq.6 contains only one single determinant, so its spin state is obvious, however for any kind of CI correction the spin situation must be taken into account. Eq.1 does not contain spin coordinates, hence both total spin operators ( $S_{op}^2$  and  $S_{op,z}$ ) must commute with it as  $[H_V + H_{ne} + a H_{ee}, S_{op}^2 \text{ or } S_{op,z}] = 0$ . The  $\Psi_k$  (exact not-single determinant eigenfunction,  $a=1$ ) and single determinant  $Y_k$  ( $a=0$ ) are also eigenfunctions, for the latter  $S_{op}^2 Y_k = S(S+1) Y_k$  and  $S_{op,z} Y_k = M_S Y_k$ , where  $S$  and  $M_S$  are the spin quantum numbers as  $S = \sum_{i=1,\dots,N} s_i$ . As usual, e.g. for a singlet state molecule, those  $Y_k$  determinants must be eliminated from the determinant expansion which are not singlets ( $M_S \neq 0$ ). The spin algebra [1] is the same for  $\{Y_k\}$  and  $\{S_k\}$ . For example, the two simplest spin-adapted cases for even  $N$  in  $Y_0$  obtained from HF-SCF/basis/ $a=0$ : the doubly excited singlet  $Y_{p(\alpha)p(\beta)r(\alpha)r(\beta)}$ , wherein  $(\alpha, \beta)$  electron pair from  $p$  orbital below LUMO are promoted to  $r$  orbital over HOMO with the same  $(\alpha, \beta)$  spin configuration as indicated in brackets, and the singly excited singlet configuration is  $2^{-1/2}(Y_{p(\alpha)r(\alpha)} + Y_{p(\beta)r(\beta)})$ , in the latter the two terms alone are also diagonal elements, but not pure spin states.

## Generalization of Brillouin’s theorem with coupling strength parameter

Conditions from above: The  $y_k(a)$  is the exact  $k^{\text{th}}$  ground ( $k=0$ ) or excited ( $k>0$ ) state solution of Eq.1  $\Rightarrow y_k(a=0)$  has single determinant form, while  $y_k(a \neq 0)$  does not; the  $\Psi_k \equiv y_k(a=1)$  are the physical wave functions of a molecular system. The single determinants  $Y_k \equiv y_k(a=0)$  are exact solutions from HF-SCF/basis/ $a=0$  (w. basis set error), and HF-SCF/basis/ $a=1$  provides the famous energy optimized single determinant approximation  $S_0 \approx \Psi_0$  (w. basis set and correlation error), along some lowest lying (crudely estimated) excited states  $S_k$ . The  $s_0(a)$  single Slater determinants from HF-SCF/basis/ $a$  calculation provides  $y_0(a) \approx s_0(a)$ , particularly,  $y_0(a=0) = s_0(a=0) \equiv Y_0$  and  $\Psi_0 \approx s_0(a=1) \equiv S_0$

holds. From lowest lying state  $Y_0$  or  $S_0$ , one can make singly excited Slater determinant [1] basis elements by replacing a spin-orbital HOMO level or below (call it b) to a spin-orbital LUMO level or higher (call it r), denoted as  $Y_{0,b}^r$  and  $S_{0,b}^r$ , resp..

Brillouin's theorem (1934) states that  $\langle S_0 | H(a=1) | S_{0,b}^r \rangle = 0$  as a consequence of the HF-SCF/basis/a=1 algorithm [1]. For this reason, extending  $S_0$  with only singly excited determinants to improve for  $\Psi_0$  or improve for  $\Psi_0$  and estimate  $\Psi_1$  is impossible, the doubly excited determinants  $S_{0,bc}^{rs}$  are necessary and are the most important corrections to  $\Psi_0$ , more exactly the  $\{S_0, \{S_{0,b}^r\}, \{S_{0,bc}^{rs}\}\}$  basis set. (Although these Brillouin matrix elements are zero, the singly excited  $S_{0,b}^r$  do have an effect on  $\Psi_0$  via Hamilton matrix elements as  $\langle S_{0,b}^r | H(a=1) | S_{0,bc}^{rs} \rangle$ .)

A trivial extension of Brillouin's theorem for cases HF-SCF/basis/a (which approximates  $y_0(a)$  by single determinant  $s_0(a)$ ) is formally the same, that is

$$\langle s_0(a) | H_V + H_{ne} + aH_{ee} | s_{0,b}^r(a) \rangle = 0, \quad (8)$$

the proof is the same as for  $a=1$  [1]. Eq.8 for  $a=0$  and its generated  $\{Y_k\}$  eigenfunction set (as a newly introduced candidate basis set for CI treatment) tells only triviality such as  $\langle Y_0 | H_V + H_{ne} | Y_{0,b}^r \rangle = 0$ , and the more general  $\langle Y_{k'} | H_V + H_{ne} | Y_k \rangle = 0$  is in Eq.7 with  $a=0$  for  $k' \neq k$ , where indices  $k$  and  $k'$  count the ground ( $Y_0$ ), singly ( $Y_{0,b}^r$ ), doubly ( $Y_{0,bc}^{rs}$ ), ... n-touply excited Slater determinants as well, because  $Y_k$ 's are orto-normal eigenfunctions. Like Hund's rule annihilates at  $a=0$  (not detailed here), Brillouin's theorem becomes a triviality, because  $s_0(a=0)$  becomes equal to  $Y_0$ , that is, an approximate form becomes an exact form. Eq.8 for eigenvalues trivially yields  $\langle y_{k'}(a) | H_V + H_{ne} + aH_{ee} | y_k(a) \rangle = 0$  also for the wider range  $k' \neq k$ , because  $y_k(a)$ 's are orto-normal eigenfunctions. The Brillouin theorem (the original, wherein  $a=1$  in Eq.8) and its extension (here, with  $a \neq 1$  in Eq.8), wherein "a" can be any tells us more, because  $s_0(a)$  and  $s_{0,b}^r(a)$  are not eigenfunctions of  $H_V + H_{ne} + aH_{ee}$ , yet (and this is the point in Brillouin theorem) these matrix elements are still zero, a characteristic property from the HF-SCF/basis/a algorithm.

The right hand side of Eq.7 is zero if  $a=0$ , or zero if  $Y_{k'}$  or  $Y_k$  differ in three or more spin-orbits [1]. For example, with  $a \neq 0$  in Eq.7, the  $Y_{0,bcde}^{rspq}$  and  $Y_{0,bcde}^{rsvw}$  differ in only two spin-orbits, and do not yield zero for the right hand side of Eq.7. In this way, Eq.8 reduces to sub-cases of Eq.7 if  $a=0$ , but Eq.7 with  $a \neq 0$  tells us even more than Eq.8, the reason being that the operator in Eq.8 and in wave functions have the same "a" values, while in Eq.7 the operator contains a value of "a", but the wave function is  $Y_k \equiv y_k(a=0)$  for  $k$  and  $k'$  i.e., two different "a" values are involved. An important consequence of this is that, for Eq.1, the  $\{Y_0, \{Y_{0,b}^r\}\}$  truncated basis set generated by  $a=0$  (using the minimal, singly excited ones) can already be used as a basis to estimate  $\Psi_0$  better than e.g., Eq.3, even to estimate  $\Psi_1$  also by the eigenvectors of the Hamiltonian matrix. This means that, it can provide the large part of correlation energy, and the doubly excited determinants do not have to be calculated to save computer time and disc space unless one needs more accurate results or higher excited states. Again, in the literature the CI calculation is based on HF-SCF/basis/a=1 generated  $\{S_0, \{S_{0,b}^r\}, \{S_{0,bc}^{rs}\}\}$  or a higher basis set to solve Eq.1 with  $a=1$ , while here, we are talking about the HF-SCF/basis/a=0 generated  $\{Y_0, \{Y_{0,b}^r\}\}$  or higher basis set to solve Eq.1 with  $a=1$ .

## Appendix

1.: The ( $\approx 1\%$  non-negligible) error,  $E_{corr}$ , of HF-SCF stems from the use of one single Slater determinant ( $S_0$ ) to approximate the ground state wave function ( $\Psi_0$ ) originating from  $a \neq 0$  particularly  $1/r_{ij}$ , and it includes the exchange (x, Fermi hole) error and correlation (c, Coulomb hole) error ( $E_{corr} := E_{xc} < 0$ ) in calculating electron-electron repulsion as  $\langle \Psi_0 | H_{ee} | \Psi_0 \rangle \approx \langle S_0 | H_{ee} | S_0 \rangle$ . We note that there is another error stemming from the use of  $S_0$  in calculating the kinetic energy as  $\langle \Psi_0 | H_V | \Psi_0 \rangle \approx \langle S_0 | H_V | S_0 \rangle$ , that is about a magnitude less than  $E_{xc}$  and has an opposite sign. Furthermore, physicists divide this problem as  $E_{corr} := E_x + E_c < 0$ , where the  $E_x > 0$  accounts for the error from  $\langle S_0 | H_V | S_0 \rangle$  and  $E_c (< -E_x < 0)$  from  $\langle S_0 | H_{ee} | S_0 \rangle$ .

2.: For even further relations, one can start from the variation principle: Let the normalized solution  $Y_0$  be a trial for Eq.1 at  $a=1$ :  $E_{electr,0} \leq \langle Y_0 | H(a=1) | Y_0 \rangle = \langle Y_0 | H_{ee} | Y_0 \rangle + \langle Y_0 | H_V + H_{ne} | Y_0 \rangle = \langle Y_0 | H_{ee} | Y_0 \rangle + e_{electr,0}$ . The reverse situation, when  $\Psi_0$ , the solution at  $a=1$ , is a trial function for  $a=0$ , one gets the simpler  $e_{electr,0} \leq \langle \Psi_0 | H_V + H_{ne} | \Psi_0 \rangle$ . Equality holds for both in the trivial case  $N=1$ , because there  $\Psi_0(N=1) = Y_0(N=1)$ , since the  $H_{ee}=0$ . From Eq.1:  $\langle \Psi_0 | H(a=1) | \Psi_0 \rangle = \langle \Psi_0 | H_V + H_{ne} | \Psi_0 \rangle + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle = E_{electr,0}$ , and the right hand side is majored by the first one as  $\langle \Psi_0 | H_V + H_{ne} | \Psi_0 \rangle + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle \leq e_{electr,0} + \langle Y_0 | H_{ee} | Y_0 \rangle$ , and with second, one obtains  $\langle \Psi_0 | H_{ee} | \Psi_0 \rangle \leq \langle Y_0 | H_{ee} | Y_0 \rangle$ . The counterpart comes with an extension as  $e_{electr,0} + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle \leq \langle \Psi_0 | H_V + H_{ne} | \Psi_0 \rangle + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle = \langle \Psi_0 | H(a=1) | \Psi_0 \rangle = E_{electr,0}$  which is  $E_{electr,0} \geq e_{electr,0} + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle$ . In summary the full relation is

$$e_{electr,0} < (e_{electr,0} + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle) \leq E_{electr,0} = (e_{electr,0} + \langle \Psi_0 | H_{ee} | \Psi_0 \rangle) / \langle \Psi_0 | Y_0 \rangle \leq (e_{electr,0} + \langle Y_0 | H_{ee} | Y_0 \rangle), \quad (9)$$

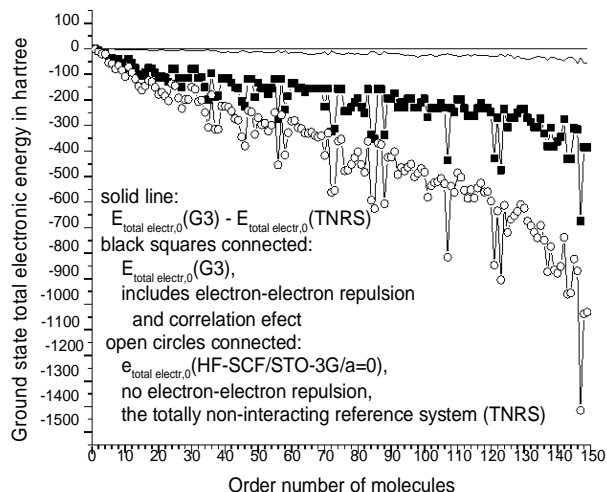
which extends as  $\langle \Psi_0 | H_{ee} | \Psi_0 \rangle \leq \langle \Psi_0 | H_{ee} | Y_0 \rangle / \langle \Psi_0 | Y_0 \rangle \leq \langle Y_0 | H_{ee} | Y_0 \rangle$ .



One other expression stemming from the variation principle has to be emphasized: The  $S_0$  from HF-SCF/basis/a=1 for Eq.1 is energetically better than  $Y_0$  from HF-SCF/basis/a=0, when one uses this  $Y_0$  for Eq.1 at a=1, that is,

$$E_{\text{electr},0} = \langle S_0 | H(a=1) | S_0 \rangle + E_{\text{corr}} < \langle S_0 | H(a=1) | S_0 \rangle \leq e_{\text{electr},0} + (N(N-1)/2) \langle Y_0 | r_{12}^{-1} | Y_0 \rangle, \quad (10)$$

where the equality may come up when small e.g., STO-3G basis set is used. The error (correlation energy) of the middle part in Eq.10 with  $S_0$  stems from the fact that  $\Psi_0$  is approximated with incorrect wave function form, namely with single determinant  $S_0$ ; but at least the LCAO coefficients vary slowly between  $Y_0(a=0)$  and  $S_0(a=1)$ . (Again, the LCAO parameters in correct functional form  $Y_0$  come from solving Eq.1 at a=0 numerically, while in the incorrect functional form  $S_0$  the LCAO parameters come from the energy minimization of  $\langle S_0 | H(a=1) | S_0 \rangle$  for Eq.1, restricted by the known ortho-normalization for MOs in both.)



**FIGURE 1.** The 150 neutral test molecules from the G3 set are chosen as increasing N, e.g. 1: H<sub>2</sub>, 10: OH radical, 20: CO, 30: C<sub>2</sub>H<sub>5</sub> radical, 40: allene (C<sub>3</sub>H<sub>4</sub>), 50: aziridine, 60: (CH<sub>3</sub>)<sub>2</sub>NH, 70: glyoxal, 80: acetone, 90: methyl ethyl ether, 100: twist C<sub>5</sub>H<sub>10</sub>, 110: n-pentane, 120: N-methyl pyrrole, 130: 3-methyl pentane, 140: CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)NO<sub>2</sub>, 147: C<sub>2</sub>F<sub>6</sub>, 148: naphthalene, 149: azulene (C<sub>10</sub>H<sub>8</sub>).

The shape of the curve itself has no particular mean, the important message is that the two curves (black squares and open circles) run together like the same fingerprint.

The related curve for open circles in Fig.1 with larger 6-31G\*\* basis set would yield lower energy values by about 2% (basis set error improvement), and would be almost at the same position for eyes, not plotted. Solid line is the deviation  $E_{\text{total_electr},0}(\text{G3}) - E_{\text{total_electr},0}(\text{TNRS})$  via first approximation in Eq.3 which brings the open circle values (a=0 in Eq.1 with small basis set error) remarkably back to black square ones (a=1 in Eq.1 with G3 estimation), it is also the approximate error of the (1,1) element of the CI matrix in Eq.5.

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